# Lecture topics

(1) Class exercise: work out by qualitative reasoning how $U = U(T)$, $C_V = C_V(T)$ given qualitative dependence of entropy curve $S = S(U)$ for paramagnet

(2) Complete derivation of multiplicity $\Omega(U, V, N)$ for monoatomic ideal gas

(3) Discuss implications of formula $\Omega$ for ideal gas

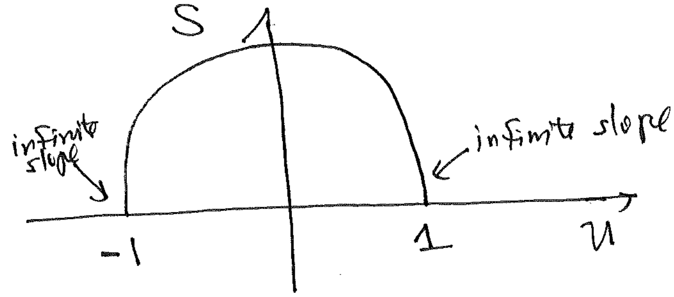
- $\Omega(U,V,N)$ very sharply peaked about equil values
- Sackur-Tetrode equation $S = S(U, V, N)$
- Entropy change for isothermal process implies $\Delta S = \frac{Q}{T}$
- Entropy of mixing, Gibb's paradox

(4) Measuring entropy experimentally via heat capacities

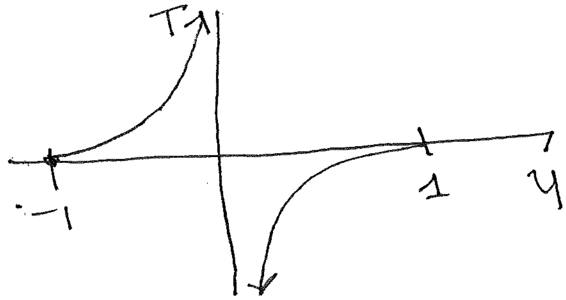
(5) Third law of thermodynamics: $S(T=0) = 0 \Rightarrow C_V, C_P \to 0$ as $T \to 0$

Class exercise: deducing qualitative insights $u=u(T)$, $C=C(T)$ from given entropy curve $S=S(u)$

Assume

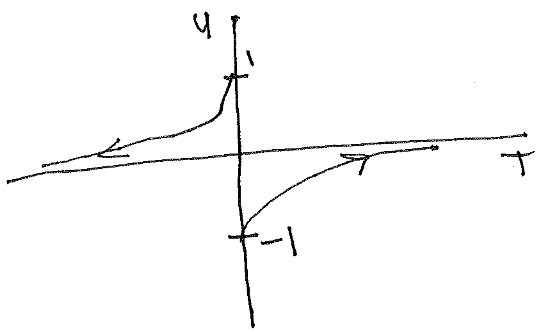



Deduce: (a)

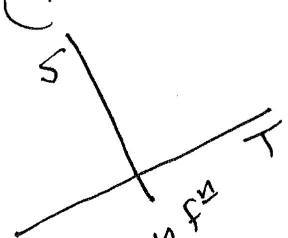



$\frac{1}{T}=\frac{dS}{du}$

(b)

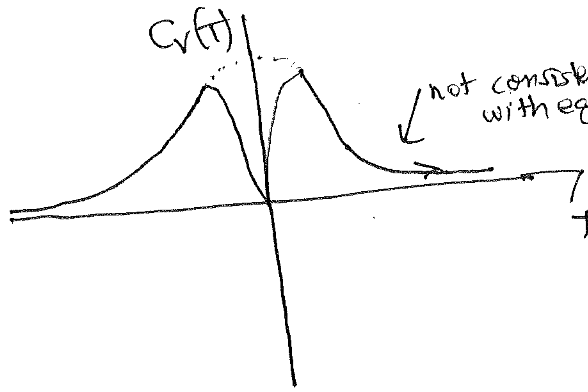



(d)




entropy as fn of T?

(c)




$C_V=\frac{du}{dT}$

not consistent with equipartition.

$C_V \propto \frac{1}{T^2}$ as $T\to\infty$

For this last curve, use fact we show later that $C_V(T)\to 0$ as $T\to 0$

Back to discussion of $\Omega(U,V,N)$ for monoatomic gas of $N$ identical atoms in isolated volume $V$, with fixed total energy $U$

macrostate: given values of $U, V, N$

microstate: 6N numbers consisting of position, momentum

$$\{x_i, y_i, z_i, p_{x,i}, p_{y,i}, p_{z,i}\}_{i=1}^{N}$$

momentum more fundamental than velocity since $\vec{p}$ but not $\vec{v}$ shows up in quantum mechanics

Reason heuristically to estimate $\Omega$, guess how it may depend on various quantities.

Consider case for $N=1$, one atom

center of mass $(x,y,z)$ can be anywhere in volume, and bigger volume implies more locations, so guess

$$\Omega(U, V, N=1) \propto V$$

$0 \le x \le L_x$
$0 \le y \le L_y$
$0 \le z \le L_z$
$V = L_x L_y L_z$

energy conservation implies

$$U = \frac{\vec{p}^{\,2}}{2m} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)$$

or $$p_x^2 + p_y^2 + p_z^2 = \left[\sqrt{2mU}\right]^2$$

$(p_x, p_y, p_z)$ lie on surface of sphere of radius $r = \sqrt{2mU}$

Guess that multiplicity $\Omega$ proportional to possible ways we can vary $\vec{p}$ on surface of sphere, i.e. to surface and $A_3(r)$ = area of 3D sphere of radius $r = \sqrt{2mU}$

$$\Omega(U, V, N=1) \propto V A_3(\sqrt{2mU})$$

This looks implausible, right side is finite but clearly volume $V$ and area $A_3(\sqrt{2mU})$ correspond to continuum of possible positions $\vec{x}$ and momenta $\vec{p}$, so $\Omega$ should be infinite.

One way out is to assume finite experimental resolution, $\Delta x$, $\Delta p$, when measuring locations and momenta, but this makes $\Omega$ depend in unsatisfying way on arbitrary resolutions

Quantum mechanics gives definitive resolution of how to obtain finite value of $\Omega(U,V,N)$ when microstates can vary continuously. Justification too complicated to explain at level of this course, requires Physics 211 discussion of the so-called "semiclassical" limit of QM as $\hbar$ becomes small, use WKB perturbation theory. So let's just assume result of this analysis.

Semi-classical limit of quantum mechanics says that uncertainty principle

$$\Delta x \, \Delta p_x \gtrsim h$$
$$\Delta y \, \Delta p_y \gtrsim h$$
$$\Delta z \, \Delta p_z \gtrsim h$$

leads to a quantization of "phase space" or "state space", the space consisting of points $(x, y, z, p_x, p_y, p_z)$ that give state of single particle.

Multiplying the above 3 inequalities gives

$$\frac{dx\, dy\, dz \cdot dp_x\, dp_y\, dp_z}{h^3} \gtrsim 1$$

i.e. we can think of phase space as broken up into little 6-dimensional cubes of size $h^3$

$$\Omega(U, V, 1) = \int_x \int_y \int_z \int_{dp_x} \int_{dp_y} \int_{dp_z} \frac{dx\,dy\,dz \;\; dp_x\,dp_y\,dp_z}{h^3}$$

The integrals over $dx, dy, dz$ lead to volume $L_x L_y L_z = V$

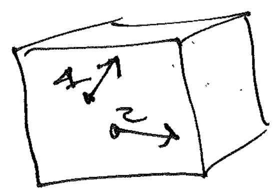
The integrals over $dp_x\, dp_y\, dp_z$ more complicated because the triple integrals are constrained, they go over surface of sphere $p_x^2 + p_y^2 + p_z^2 = 2mU$, but they end up being proportional to $A_3(\sqrt{2mU})$

Result of previous conclusion:

$$\Omega(U, V, N=1) = \frac{V A_3(\sqrt{2mU})}{h^3}$$

gives precise and correct multiplicity

<u>Case N = 2</u>




Position $\vec{x}_1$ of particle 1 independent of $\vec{x}_2$ so guess

$$\Omega(U, V, N=2) \propto V^2$$

Momentum $\vec{p}_1$ of particle 1 is <u>not</u> independent of $\vec{p}_2$ because for <u>isolated</u> system

$$U = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} = \frac{1}{2m}\left[p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2\right]$$

or

$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 = \left[\sqrt{2mU}\right]^2$$

This is surface of 6-dimensional hypersphere. Conclude

$$\Omega(U, V, N=2) = \frac{V^2 A_6(\sqrt{2mU})}{(h^3)^2}$$

notice we need twice as many h's to count cubes in bigger phase space

# Implications of Identical Particles for $\Omega(U,V,N)$

Conclusion $\Omega(U,V,N=2) = \frac{V^2 A_6(\sqrt{2mU})}{(h^3)^2}$ is wrong

for identical atoms, it overcounts the microstates by including microstates with two particles exchanged $(\vec{x}_1, \vec{p}_1) \leftrightarrow (\vec{x}_2, \vec{p}_2)$

Correct formula is

$$\Omega(U,V,N=2) = \frac{V^2 A_6(\sqrt{2mU})}{(h^3)^2} \frac{1}{2!}$$

General case is then

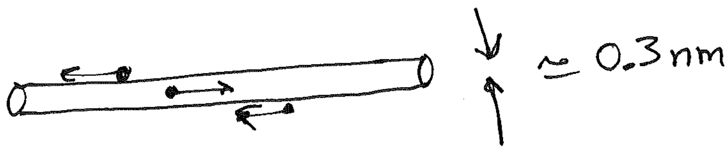
$$\boxed{\Omega(U,V,N) = \underbrace{\frac{1}{N!}}_{\text{to prevent overcounting}} \frac{V^N A_{3N}(\sqrt{2mU})}{h^{3N}}}$$

Note: are particles like e, p, H truly exactly identical, no hidden labels?

answer is yes, this is prediction of quantum field theory

Feynman's crazy idea: only one electron in universe, travels back in time to interact with itself, would explain why all particles exactly identical

Class project: what is $\Omega(U, L, N)$ for ideal gas on one-dimensional carbon nanotube of length $L$?




$$\Omega(U, L, N) = \frac{L^{?} A_{?}(?)}{h^{?}} \times ?$$

## Surface area of d-dimensional hypersphere of radius r

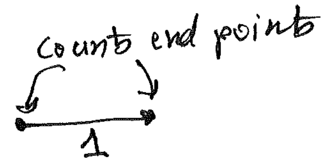
There is an analytical formula

$$A_d(r) = \frac{2 \cdot \pi^{d/2} \cdot r^{d-1}}{\Gamma\left(\frac{d}{2}\right)} \qquad \Gamma\left(\tfrac{d}{2}\right) = \left(\tfrac{d}{2}-1\right)!$$

~~where~~ where $\Gamma(x)$ is Euler Gamma $f^n$

Some values:

$$A_1(1) = \frac{2 \cdot \pi^{1/2}}{\Gamma\left(\frac{1}{2}\right)} = 2 \checkmark$$




$$A_2(1) = \frac{2 \cdot \pi}{\Gamma(1)} = 2\pi \checkmark$$

$$A_3(1) = \frac{2 \cdot \pi^{3/2}}{\Gamma\left(\frac{3}{2}\right)} = \frac{2 \cdot \pi^{3/2}}{\frac{3}{2}\Gamma\left(\frac{1}{2}\right)} = 4\pi \checkmark$$

In homework, you calculate $A_4(1)$, $A_5(1)$, plot $A_d(1)$ vs $d$

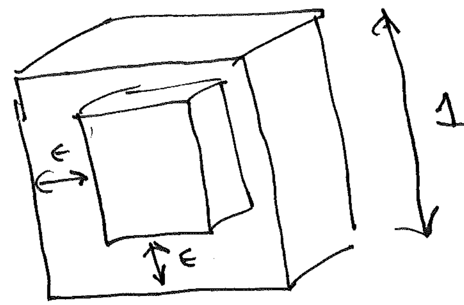
Outline of derivation:

$$\underbrace{\int_{-\infty}^{\infty} e^{-x_1^2}dx_1}_{\sqrt{\pi}} \times \underbrace{\int_{-\infty}^{\infty} e^{-x_2^2}dx_2}_{\sqrt{\pi}} \cdots \times \underbrace{\int_{-\infty}^{\infty} e^{-x_d^2}dx_d}_{\sqrt{\pi}} = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} e^{-(x_1^2+x_2^2+\dots+x_d^2)} dx_1 \cdots dx_d$$

$$\pi^{d/2} = \int_0^{\infty} dr \cdot e^{-r^2} \cdot \underbrace{A_d(1) \cdot r^{d-1}} = A_d(1) \int_0^{\infty} e^{-r^2} r^{d-1} dr$$

change variable $t = r^2$ to express in terms of $\Gamma$

Paradox: high-dimensional volumes are mainly surfaces




Consider $d$-dimensional hypercube of length 1, volume

$$V_d = 1 \times 1 \times \cdots \times 1 = 1$$

Consider concentric smaller hypercube, of side $1-2\epsilon$

$$V = (1-2\epsilon) \times (1-2\epsilon) \cdots \times (1-2\epsilon) = (1-2\epsilon)^d$$

$(0.99)^{100} \simeq 0.4 \Longrightarrow$ 60% of volume of unit hypercube lies within 0.005 of surface!

$(0.99)^{10^{23}} \simeq 0 \Longrightarrow$ cube is all surface

# Formula For Multiplicity

$$\Omega(U,V,N) = \frac{1}{N!}\,\frac{V^N}{h^{3N}}\cdot\frac{\overset{\text{drop}}{2}\cdot\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)}\left(\sqrt{2mU}\right)^{3N\overset{\text{drop}}{-1}}$$

For N large, can simplify:

$$\Gamma\left(\tfrac{3N}{2}\right) = \left(\tfrac{3N}{2}-1\right)! \simeq \left(\tfrac{3N}{2}\right)! \quad \text{for } N \gg 1$$

$$\boxed{\begin{aligned} &\Omega(U,V,N) \simeq f(N)\,V^N\,U^{3N/2} \qquad N \gg 1 \\ &f(N) = \left(\frac{2\pi m}{h^2}\right)^{3N/2}\frac{1}{\underset{\uparrow}{N!}\left(\frac{3N}{2}\right)!} \end{aligned}}$$

from particles being identical

$$S = k\ln\Omega = k\ln\left[\left(\frac{2\pi m}{h^2}\right)^{3N/2} U^{3N/2}\,V^N\,\frac{1}{N!\left(\frac{3N}{2}\right)!}\right]$$

$$\simeq k\left[N\ln V + N\ln\left[\left(\frac{2\pi m U}{h^2}\right)^{3/2}\right] - N\ln N + N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2}\right]$$

$$\boxed{S \simeq Nk\left[\frac{5}{2} + \ln\left(\frac{V}{N}\left(\frac{4\pi m}{3h^2}\cdot\frac{U}{N}\right)^{3/2}\right)\right]}$$

$N \gg 1$
ideal gas

Sackur-Tetrode equation for entropy of monoatomic gas
~1912